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**(54) Non-chrome final rinse for phosphated metal**

### Chromfreie Abschlussspülung für phosphatiertes Metall

#### Rinçage final exempt de chrome pour métal phosphaté

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**Description**

The present invention relates to non-chrome passivating compositions which are employed as final rinses in the pretreatment of substrates. More specifically, the present invention relates to non-chrome final rinse compositions containing amino acids or amino alcohols or salts thereof in combination with transition metal compounds.

**Brief Description of the Prior Art**

In the pretreatment of substrates, particularly by phosphate conversion coating, final rinses are employed to enhance the corrosion resistance of the pretreated substrate. Chromic acid rinses are usually employed as final rinses. Given the present environmental and safety climate, it is now deemed desirable to replace chromic acid rinses.

EP-A-0 410 497, which is prior art under the terms of Article 54(3) and (4) EPC, discloses the passivating aftertreatment of phosphated steel surfaces with an aqueous non-chrome rinse composition being based on aluminum fluozirconate and having a total concentration of Al+Zr+F of from 0.1-2.0 g/l and a pH of from 3-5, wherein the adjustment of pH of the said solution is preferably carried out using cations of volatile bases including ammonium, ethanolammonium and di- and tri-ethanolammonium. An example is given in which the composition contains 0.026 g/l ammonia.

U.S. Patent 3,695,942 discloses non-chrome final rinses comprising an aqueous zirconium rinse solution consisting essentially of a soluble zirconium compound which is typically in the form of an alkali metal or ammonium salt of zirconium hydroxy carboxylate such as zirconium acetate or zirconium oxalate.

U.S. Patent 3,895,970 discloses non-chrome final rinses comprising an acidic solution of certain fluoride ions obtained from calcium, zinc, zinc aluminum, titanium, zirconium, nickel, ammonium fluoride, hydrofluoric acid, fluoboric acid or a mixture thereof.

U.S. Patent 4,457,790 discloses a treatment composition comprising a metal ion selected from the group consisting of titanium, hafnium and zirconium and a mixture thereof, and an effective amount of a soluble or dispersible treatment compound selected from the group consisting of a polymer which is a derivative of a polyalkenylphenol.

However, most non-chrome rinses have not risen to the level of commercially useful final rinses. Even though somewhat successful, the prior art non-chrome rinses tend not to consistently match the performance of chrome rinses. By the present invention there is provided an improved non-chrome final rinse composition.

**Summary of the Invention**

In accordance with the foregoing, the present invention relates to a water-based non-chrome passivating composition comprising:

(a) an amino compound which is an amino acid or an amino alcohol at a level of 50 to 100,000 parts per million, said amino acid being selected from glycine, sarcosine, iminodiacetic acid, leucine, tyrosine, taurine, N-methyl taurine, aminobenzoic acid, gamma-aminobutyric acid and salts thereof; said amino alcohol being selected from imidazoline, oleyl imidazoline, choline, triethanolamine, diethanol glycine, ethanol diglycine, 2-amino-2-ethyl-1,3-propanediol and amino propanol and salts thereof, and

(b) a group IVB transition metal compound selected from compounds of Ti, Zr and Hf; and further optionally

(c) acids or bases for adjusting the pH, and/or

(d) organic solvent.

In a presently preferred embodiment of the invention, the amino compound is sarcosine or glycine and the transition metal compound is a zirconium compound such as fluozirconic acid and its salts.

As a final rinse, the preferred compositions of the present invention have been found to perform at least as well as the commonly used chrome-containing final rinses without the associated problem of chromic acid. This and other aspects of the invention are more fully described hereinbelow.

**Detailed Description of the Invention**

As aforeslated, the water-based non-chrome passivating composition of the present invention comprises

(a) an amino compound which is an amino acid or an amino alcohol at a level of 50 to 100,000 parts per million, said amino acid being selected from glycine, sarcosine, iminodiacetic acid, leucine, tyrosine, taurine, N-methyl tau-

rine, aminobenzoic acid, gamma-aminobutyric acid and salts thereof; said amino alcohol being selected from imidazoline, oleyl imidazoline, choline, triethanolamine, diethanol glycine, ethanol diglycine, 2-amino-2-ethyl-1,3-propanediol and amino propanol and salts thereof, and

5 (b) a group IVB transition metal compound selected from compounds of Ti, Zr and Hf; and further optionally  
 (c) acids or bases for adjusting the pH, and/or  
 (d) organic solvent.

10 The pH of the composition can be from about 2.0 to 8.0 and preferably from about 3.5 to 6.0, at a temperature of 15 to 100°C and preferably 30 to 60°C.

Preferably the amino compound is present at a level of about 100 to 10,000 parts per million.

15 As indicated above, the composition of the invention contains a group IVB transition metal compound selected from compounds of titanium, zirconium and hafnium. More particularly, said compounds may be selected from compounds of zirconium and titanium.

20 Typical examples of the zirconium compound can be selected from the group consisting of acids or acid salts of zirconium such as alkali metal or ammonium fluozirconates, zirconium carboxylates and zirconium hydroxy 35 carboxylates, e.g., hydrofluozirconic acid, zirconium acetate, zirconium oxalate, ammonium zirconium glycolate, ammonium zirconium lactate, ammonium zirconium citrate or the like. A preferred zirconium compound can be fluozirconic acid or its salts. A preferred example of the titanium compound can be fluotitanic acid or its salts. A preferred example of the hafnium compounds is hafnium nitrate.

The transition or rare earth metal compound is present at a level of 10 to 10,000 parts per million and preferably at a level of about 25 to 1,500 parts per million.

25 In the process of preparing the non-chrome rinse composition of this invention, the amino acid or amino alcohol can be blended with the transition metal compound in the presence of water. Other ingredients that can be employed herein can be acids such as nitric, acetic, and sulfamic and bases such as sodium hydroxide, ammonia and potassium hydroxide. Such acids and bases would be used to adjust the pH of the bath. It may also be desirable to include an organic solvent in the bath.

30 In the practice of the invention, the non-chrome final rinse composition is applied to a substrate that had been pretreated by conversion coating with, say, a phosphate conversion coating. The rinse composition can be applied by spray or immersion techniques. The rinse time should be as long as would ensure sufficient wetting of the surface with the rinse composition. Typically, the rinse time is from about 5 sec. to 10 min. and preferably from 15 sec. to 1 min. over a temperature range of about 15°C to 100°C and preferably 30°C to 60°C. After the final rinse, the metal is usually dried either by air drying or forced drying. In some instances, a water rinse is employed after the final rinse. A protective or decorative coating is usually applied to the substrate after it had been pretreated as set forth above.

35 It has been found that metal substrates that have been pretreated by phosphate conversion coating followed by a final rinse with the preferred non-chrome rinse compositions of this invention have been found to exhibit corrosion resistance and adhesion which is at least equivalent to the results obtained in the instance of using chrome containing final rinses. This and other aspects of the invention are further illustrated by the following non-limiting examples.

### Examples

40 The following examples show the non-chrome rinse of this invention, the methods of preparing and using the same, and the comparison of the claimed rinses with art-related compositions.

45 The panels treated in the examples that follow have all been pretreated in the following process sequence unless otherwise noted in the example.

50 Prewipe with "CHEMKLEEN 340", which is a mildly alkaline prewipe cleaner available from Chemfil Corporation (Chemfil).

55 Stage #1 "CHEMKLEEN 48L" which is an alkaline cleaner available from Chemfil (Alkaline clean), spray 1% by volume at 57-60°C (135-140°F) for 1 minute.

Stage #2 Hot water rinse, by spraying at 57-60°C (135-140°F), for 30 seconds.

55 Stage #3 CHEMFOS 158 (iron phosphate conversion coating available from Chemfil), by spraying Total Acid 11.0-13.0 ml (3.8% by volume) Acid consumed titration 0.3-0.7 ml 63-66°C (145-150°F) for 1 minute

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Stage #4 Ambient water rinse, by spraying at ambient temperature for 30 seconds

Stage #5 Final or Post rinse, by immersion for 30 seconds (chrome rinse ambient, non-chrome 49°C (120°F))

5 Stage #6 Deionized water rinse, by spraying at ambient temperature

All final rinses were adjusted to the indicated pH in the Tables to follow, with solutions of sodium hydroxide and/or nitric acid.

10 All the panels were painted with DURACRON 200 which is an acrylic type coating available from PPG Industries, Inc. (PPG). Panels were scribed diagonally to form a large X and placed in salt spray chambers as per ASTM B117. The panels were then removed and rated as follows: One diagonal scribe was rubbed with a mild abrasive pad to remove any excess rust. Tape was applied to the scribe and then removed vigorously to pull off any delaminated paint. Three 2.5 cm (one-inch) sections each on the top and the bottom of the diagonal were marked off. The maximum width of paint delamination in each 2.5 cm (one-inch) section was measured, and these six measurements were averaged to give the 15 rating of the panel.

### Example 1

20 Zirconium was added as Hydrofluozirconic acid ( $H_2ZrF_6$ ), produced by Cabot Company, and sarcosine were added as a 40% by weight solution of sodium sarcosinate, produced by W. R. Grace Co. Panels were tested in neutral salt spray for 504 hours (3 weeks). The results for these tests are shown in the following Table I.

TABLE I

Panel set #	Zirconium (ppm)	Sarcosine (ppm)	pH	creep (mm)
0		Deionized water blank	13, 15	
16		Chrome control 0.25% CS 20	4.06	5, 6
25	100	(Zr-only control; CHEMSEAL 19 0.5%)	4.28	2, 3
1	175	900	4.90	2, 1
3	175	100	4.64	3, 1
6	100	900	3.86	4, 4
10	175	500	3.81	3, 4
13	100	500	4.79	3, 2

### Example 2

The compositions shown in Table II were tested in a manner similar to Example 1. The results are shown in Table II.

TABLE II

Panel set #	Zirconium (ppm)	oleyl imidazoline (ppm)	pH	creep (mm)
0		Deionized water blank	14, 14	
19		Chrome control (0.25% CHEMSEAL 20)	3, 3	
1	175	900	4.47	5, 3
5	100	900	5.03	4, 2
7	100	100	5.09	2, 2
9	175	500	4.95	2, 2
14	100	500	4.45	3, 4
17	100	500	5.55	2, 5

### Examples 3-4

55 The compositions listed in Tables III and IV below were tested in a manner similar to Example 1. All compounds were tested at 500 ppm except where noted. All non-chrome final rinses were run at 49°C (120°F).

A significant difference between the previous Tables and Tables III, IV and V to follow is that the test panels were pulled from test, taped, and rated on a weekly basis. This is a more severe test than only taping at the end of the test.

Results at the end of three weeks are reported below, except that which were removed earlier than three weeks are noted.

TABLE III

Compound tested	Zirconium (ppm)	pH	creep (mm)
CHEMSEAL 20, 0.25%	---	4.50	3, 3
Deionized water (blank)	---	----	fail (2 wks)
CHEMSEAL 19, 0.5%	100	4.00	10, 8
Triethanolamine	0	4.00	14, 25 (2 wks)
Triethanolamine	100	3.95	5, 5

TABLE IV

Compound tested	Zirconium (ppm)	pH	creep (mm)
CHEMSEAL 20, 0.25%	---	4.08	4, 6
Deionized water (blank)	---	----	fail (2 wks)
CHEMSEAL 19, 0.5%	100	4.16	10, 8
Tyrosine (814 ppm)	100	4.02	9, 7
Glycine (338 ppm)	100	4.07	5, 7
o-Aminophenol-4-sulfonamide	0	4.03	13, 15 (2 wks)
o-Aminophenol-4-sulfonamide	100	3.85	7, 6
Choline	0	3.95	12, 13 (2 wks)
Choline	100	4.03	5, 9
2-amino-2-ethyl-1,3-propanediol	0	4.05	fail (2 wks)
2-amino-2-ethyl-1,3-propanediol	100	3.92	7, 6

#### Example 5

Table V shows the comparative performance of a version of the novel non-chrome rinse on a cleaner-coater iron phosphate coating, which is inherently poorer coating. The process sequence for these panels differed in that the prewipe and stages 1 and 2 were eliminated, and stage 3 was charged with CHEMFOS L24-D, which is an iron phosphate type cleaner-coater available from Chemfil, at 3% (total acid 5.8 ml). Other operating variables were the same.

TABLE V

Compound tested	Zirconium (ppm)	pH	creep (mm)
CHEMSEAL 20, 0.25%	---	4.22	5, 3
Deionized water (blank)	---	----	fail (2 wks)
CHEMSEAL 19, which is a zirconium only final rinse available from Chemfil	150	4.25	18, 13
Sodium Sarcosinate (500 ppm)	100	4.13	9, 7

#### Claims

1. A water-based non-chrome passivating composition comprising:

(a) an amino compound which is an amino acid or an amino alcohol at a level of 50 to 100,000 parts per million, said amino acid being selected from glycine, sarcosine, iminodiacetic acid, leucine, tyrosine, taurine, N-methyl taurine, aminobenzoic acid, gamma-aminobutyric acid and salts thereof; said amino alcohol being selected from imidazoline, oleyl imidazoline, choline, triethanolamine, diethanol glycine, ethanol diglycine, 2-amino-2-ethyl-1,3-propanediol and amino propanol and salts thereof, and

(b) a group IVB transition metal compound selected from compounds of Ti, Zr and Hf; and further optionally  
(c) acids or bases for adjusting the pH, and/or  
(d) organic solvent.

5 2. The passivating composition of claim 1 wherein the amino compound is present at a level of 100 to 10,000 parts per million.

3. The passivating composition of claim 1 wherein the group IVB transition metal compound is present at a level of 10 to 10,000 parts per million.

10 4. The passivating composition of claim 1 wherein the group IVB transition metal compound is present at a level of 25 to 1500 parts per million.

5. The passivating composition of claim 1 having a pH of 2.0 to 8.0.

15 6. The passivating composition of claim 5 having a pH of about 3.5 to 6.0.

7. The passivating composition of claim 1 wherein the group IVB transition metal is selected from zirconium and titanium.

20 8. A process for treating a phosphated metal surface comprising contacting said phosphated metal surface with a water-based non-chrome composition comprising:

25 (a) an amino compound which is an amino acid or an amino alcohol at a level of 50 to 100,000 parts per million, said amino acid being selected from glycine, sarcosine, iminodiacetic acid, leucine, tyrosine, taurine, N-methyl taurine, aminobenzoic acid, gamma-aminobutyric acid and salts thereof; said amino alcohol being selected from imidazoline, oleyl imidazoline, choline, triethanolamine, diethanol glycine, ethanol diglycine, 2-amino-2-ethyl-1,3-propanediol and amino propanol and salts thereof, and

30 (b) a group IVB transition metal compound selected from compounds of Ti, Zr and Hf; and further optionally

(c) acids or bases for adjusting the pH, and/or

(d) organic solvent.

9. The process of claim 8 wherein the amino compound is present at a level of 100 to 10,000 parts per million.

35 10. The process of claim 8 wherein the group IVB metal compound is present at a level of 10 to 10,000 parts per million.

11. The process of claim 10 wherein the group IVB metal compound is present at a level of 25 to 1500 parts per million.

12. The process of claim 8 wherein the phosphated substrate is an iron phosphated substrate.

40 13. The process of claim 8 wherein the water-based composition has a pH of about 2.0 to 8.0.

14. The process of claim 13 wherein the water-based composition has a pH of about 3.5 to 6.0.

45 15. The process of claim 8 wherein the water-based composition has a temperature of 15 to 100°C.

16. The process of claim 15 wherein the water-based composition has a temperature of 30 to 60°C.

50 **Patentansprüche**

1. Eine auf Wasser basierende, nicht chromhaltige, passivierende Zusammensetzung, die umfaßt:

55 (a) eine Aminoverbindung, die eine Aminosäure oder ein Aminoalkohol ist mit einem Niveau von 50 bis 100.000 Teilen je Million, wobei die besagte Aminosäure ausgewählt ist aus Glycin, Sarcosin, Iminodiessigsäure, Leucin, Tyrosin, Taurin, N-methyl-Taurin, Aminobenzoësäure, Gamma-Aminobuttersäure sowie Salzen hieraus und der besagte Aminoalkohol ausgewählt ist aus Imidazolin, Oleyl-Imidazolin, Cholin, Triethanolamin, Diethanol-Glycin, Ethanol-Diglycin, 2-Amino-2-ethyl-1,3-propandiol und Aminopropanol sowie Salzen hieraus und

(b) eine Übergangsmetallverbindung der IVB-Gruppe, ausgewählt aus Verbindungen von Ti, Zr und Hf, sowie außerdem optionell

5 (c) Säuren oder Basen zur Einstellung des pH-Wertes und/oder

(d) ein organisches Lösemittel.

2. Die passivierende Zusammensetzung nach Anspruch 1, in der die Aminoverbindung mit einem Niveau von 100 bis 10.000 Teilen je Million vorkommt.

10 3. Die passivierende Zusammensetzung nach Anspruch 1, in der die Übergangsmetallverbindung der IVB-Gruppe mit einem Niveau von 10 bis 10.000 Teilen je Million vorkommt.

15 4. Die passivierende Zusammensetzung nach Anspruch 1, in der die Übergangsmetallverbindung der IVB-Gruppe mit einem Niveau von 25 bis 1500 Teilen je Million vorkommt.

5. Die passivierende Zusammensetzung nach Anspruch 1 mit einem pH-Wert von 2,0 bis 8,0.

20 6. Die passivierende Zusammensetzung nach Anspruch 5 mit einem pH-Wert von ungefähr 3,5 bis 6,0.

7. Die passivierende Zusammensetzung nach Anspruch 1, in der das Übergangsmetall der IVB-Gruppe ausgewählt ist aus Zirkon und Titan.

25 8. Ein Verfahren zur Behandlung einer phosphatierten Metallocberfläche, die die Kontaktbehandlung der besagten phosphatierten Metallocberfläche mit einer auf Wasser basierenden, nicht chromhaltigen Zusammensetzung umfaßt, die folgendes einschließt:

30 (a) eine Aminoverbindung, die eine Aminosäure oder ein Aminoalkohol ist mit einem Niveau von 50 bis 100.000 Teilen je Million, wobei die besagte Aminosäure ausgewählt ist aus Glycin, Sarcosin, Iminodiessigsäure, Leucin, Tyrosin, Taurin, N-methyl-Taurin, Aminobenzoësäure, Gamma-Aminobuttersäure sowie Salzen hieraus und der besagte Aminoalkohol ausgewählt ist aus Imidazolin, Oleyl-Imidazolin, Cholin, Triethanolamin, Diethanol-Glycin, Ethanol-Diglycin, 2-Amino-2-ethyl-1,3-propandiol und Aminopropanol sowie Salzen hieraus und

35 (b) eine Übergangsmetallverbindung der IVB-Gruppe, ausgewählt aus Verbindungen von Ti, Zr und Hf, sowie außerdem optionell

(c) Säuren oder Basen zur Einstellung des pH-Wertes und/oder

(d) ein organisches Lösemittel.

40 9. Das Verfahren nach Anspruch 8, in dem die Aminoverbindung mit einem Niveau von 100 bis 10.000 Teilen je Million vorkommt.

10. Das Verfahren nach Anspruch 8, in dem die Metallverbindung der IVB-Gruppe mit einem Niveau von 10 bis 10.000 Teilen je Million vorkommt.

45 11. Das Verfahren nach Anspruch 10, in dem die Metallverbindung der IVB-Gruppe mit einem Niveau von 25 bis 1500 Teilen je Million vorkommt.

12. Das Verfahren nach Anspruch 8, in dem das phosphatierte Substrat ein eisenphosphatiertes Substrat ist.

50 13. Das Verfahren nach Anspruch 8, in dem die auf Wasser basierende Zusammensetzung einen pH-Wert von ungefähr 2,0 bis 8,0 hat.

14. Das Verfahren nach Anspruch 13, in dem die auf Wasser basierende Zusammensetzung einen pH-Wert von ungefähr 3,5 bis 6,0 hat.

55 15. Das Verfahren nach Anspruch 8, in dem die auf Wasser basierende Zusammensetzung eine Temperatur von 15 bis 100°C hat.

16. Das Verfahren nach Anspruch 15, in dem die auf Wasser basierende Zusammensetzung eine Temperatur von 30

bis 60°C hat.

**Revendications**

- 5 1. Une composition de passivation à base d'eau et exempte de chrome comprenant:
  - (a) un composé amine qui est un acide amine ou un alcool amine à un niveau de 50 à 100 000 parts par million, ledit acide amine étant sélectionné parmi glycine, sarcosine, acide iminodiacétique, leucine, tyrosine, taurine, N-méthyle taurine, acide aminobenzoïque, acide gamma-aminobutyrique et sels de ces acides; ledit alcool amine étant sélectionné parmi imidazoline, oléyle imidazoline, choline, triéthanolamine, diéthanol glycine, éthanol diglycine, 2-amino-2-éthyle-1,3-propanediol, et amino propanol et leurs sels; et
  - (b) un composé métallique de transition du groupe IVB sélectionné parmi les composés de Ti, Zr et Hf; et aussi optionnellement
  - (c) des acides ou des bases pour l'ajustement du pH, et/ou
  - (d) solvant organique.
- 20 2. La composition de passivation de la revendication 1 dans laquelle le composé amine est présent à un niveau de 100 à 10 000 parts par million.
- 25 3. La composition de passivation de la revendication 1 dans laquelle le composé métallique de transition du groupe IVB est présent à un niveau de 10 à 10 000 parts par million.
- 40 4. La composition de passivation de la revendication 1 dans laquelle le composé métallique de transition du groupe IVB est présent à un niveau de 25 à 1500 parts par million.
- 5 5. La composition de passivation de la revendication 1 ayant un pH de 2,0 à 8,0.
6. La composition de passivation de la revendication 5 ayant un pH d'environ 3,5 à 6,0.
- 35 7. La composition de passivation de la revendication 1 dans laquelle le métal de transition du groupe IVB est choisi entre le zirconium et le titane.
8. Un procédé pour traiter une surface métallique phosphatée comprenant le contact de ladite surface métallique phosphatée avec une composition à base d'eau exempte de chrome comprenant:
  - (a) un composé amine qui est un acide amine ou un alcool amine à un niveau de 50 à 100 000 parts par million, ledit acide amine étant sélectionné parmi glycine, sarcosine, acide iminodiacétique, leucine, tyrosine, taurine, N-méthyle taurine, acide aminobenzoïque, acide gamma-aminobutyrique et sels de ces acides; ledit alcool amine étant sélectionné parmi imidazoline, oléyle imidazoline, choline, triéthanolamine, diéthanol glycine, éthanol diglycine, 2-amino-2-éthyle-1,3-propanediol, et amino propanol et leurs sels; et
  - (b) un composé métallique de transition du groupe IVB sélectionné parmi les composés de Ti, Zr et Hf; et aussi optionnellement
  - (c) des acides ou des bases pour l'ajustement du pH, et/ou
  - (d) solvant organique.
- 50 9. Le procédé de la revendication 8 dans lequel le composé amine est présent à un niveau de 100 à 10 000 parts par million.
- 55 10. Le procédé de la revendication 8 dans lequel le composé métallique du groupe IVB est présent à un niveau de 10 à 10 000 parts par million.

11. Le procédé de la revendication 10 dans lequel le composé métallique du groupe IVB est présent à un niveau de 25 à 1500 parts par million.

12. Le procédé de la revendication 8 dans lequel le substrat phosphaté est un substrat phosphaté de fer.

5 13. Le procédé de la revendication 8 dans lequel la composition à base d'eau a un pH d'environ 2,0 à 8,0.

14. Le procédé de la revendication 13 dans lequel la composition à base d'eau a un pH d'environ 3,5 à 6,0.

10 15. Le procédé de la revendication 8 dans lequel la composition à base d'eau a une température de 15 à 100°C.

16. Le procédé de la revendication 15 dans lequel la composition à base d'eau a une température de 30 à 60°C.

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